

On the stupendous beauty of closure

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Abstract

Closure seems to be something rheologists would prefer to avoid. Here, the story of closure is told in such a way that one should enduringly forget any improper undertone of “uncontrolled approximation” or “necessary evil” which might arise, for example, in reducing a diffusion equation in configuration space to moment equations. In its widest sense, closure is associated with the search for self-contained levels of description on which time-evolution equations can be formulated in a closed, or autonomous, form. Proper closure requires the identification of the relevant structural variables participating in the dominant processes in a system of interest, and closure hence is synonymous with focusing on the essence of a problem and consequently with deep understanding. The derivation of closed equations may or may not be accompanied by the elimination of fast processes in favor of dissipation. As a general requirement, any closed set of evolution equations should be thermodynamically admissible. Thermodynamic admissibility comprises much more than the second law of thermodynamics, most notably, a clear separation of reversible and irreversible effects and a profound geometric structure of the reversible terms as a hallmark of reversibility. We discuss some implications of the intimate relationship between nonequilibrium thermodynamics and the principles of closure for rheology, and we illustrate the abstract ideas for the rod model of liquid crystal polymers, bead-spring models of dilute polymer solutions, and the reptation model of melts of entangled linear polymers.

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I. INTRODUCTION

The term “closure” usually comes in the combination “closure approximation,” and it is considered as a necessary evil in deriving an autonomous, or closed, set of evolution equations in an attempt to simplify or solve a problem. Employing a closure approximation, usually of unclear and uncontrollable quality, then appears as the desperate way out of a dead end.

The prototype scenario for closure approximations is the passage from probability densities to moments. The evolution of a probability density, or configurational distribution function, of a Markov process is governed by some kind of Kolmogorov forward or differential Chapman-Kolmogorov equation [Gardiner (1990); Öttinger (1996)], say a Fokker-Planck equation (or, a diffusion equation in configuration space). The goal is to derive autonomous evolution equations for a set of moments. The dilemma is that the evolution equations for the moments following from the Fokker-Planck equation involve more complicated moments than one intended to consider. Adding these more complicated moments to the list of variables does not help because their evolution involves even more complicated moments. To avoid an intractable infinite hierarchy one needs to approximate the more complicated moments in terms of the simpler moments that one actually wants to work with. Only such a closure approximation leads to an autonomous set of evolution equations for a set of moments. In rheology, a number of systems are treated by closure approximations of this type, such as *liquid-crystal polymers* [Hinch and Leal (1976); Doi (1981); Doi and Edwards (1986); Advani and Tucker III (1990); Larson (1990); Larson and Öttinger (1991); Bhave et al. (1993); Chaubal et al. (1995); Chaubal and Leal (1998); Feng et al. (1998); Ilg et al. (1999); Edwards (2002); Forest and Wang (2003); Kröger et al. (2008)], *magnetic fluids* [Martsenyuk et al. (1974); Zubarev and Iskakova (2000); Ilg and Kröger (2002)], or the nonlinear effects of *finitely extensible nonlinear elastic (FENE) springs* [Bird et al. (1980); Öttinger (1987b); Wedgewood and Öttinger (1988); Wedgewood et al. (1991); Herrchen and Öttinger (1997); Lielens et al. (1999); Yu et al. (2005); Du et al. (2005); Prabhakar and Prakash (2006)] *hydrodynamic interactions* [Öttinger (1987a); Öttinger (1989b); Zylka and Öttinger (1989); Öttinger (1989a); Wedgewood (1989); Prakash and Öttinger (1997)] and *excluded volume* [Prakash and Öttinger (1999); Prabhakar and Prakash (2002); Prakash (2002)] in dilute polymer solutions [Bird, Curtiss, Armstrong and Hassager (1987); Bird and Öttinger

(1992)]. The pioneer of closure for a dumbbell model with a nonlinear spring force law was Peterlin (1961, 1966). Experience based on a comparison of the solutions of Fokker-Planck equations and moment equations suggests that there seems to be enormous room for criticism and improvement in the closure game.

A similar closure problem arises if one starts from a probability density in a high-dimensional space and passes to a contracted lower-dimensional distribution by integrating out degrees of freedom. A classical challenge is the derivation of evolution equations for the single- and two-particle distribution functions from the Liouville equation for the probability density of a macroscopically large number of particles. For pairwise interactions, the equation for the n -particle distribution function involves also the $(n + 1)$ -particle distribution function. One thus arrives at the BBGKY hierarchy of equations for contracted distribution functions introduced independently by Bogolyubov (1946), Born and Green (1946), Kirkwood (1946), and Yvon (1937). In this context, Boltzmann's celebrated *Stoßzahlansatz*, in which the two-particle distribution function at the beginning of a collision is expressed as a product of single-particle distribution functions, is the basis for the successful derivation of a closed kinetic equation for the single-particle distribution. Also in this context, closure has led to doubts and controversy, for example, about its role in the emergence of irreversibility.

At this point, it should be quite obvious why closure is often perceived as a necessary evil and as a questionable but unavoidable mathematical trick with threateningly far-reaching consequences. Why then would anybody associate stupendous beauty with closure, as suggested in the title of this article? As illustrated above, closure has to do with the search for simplified autonomous levels of description, and *proper simplification is the key to understanding by focusing on the essence of a problem*. The search for closure, understood as the physically motivated search for simple autonomous levels of description for a given range of phenomena of interest, is at the heart of developing insightful theories leading to fundamental understanding and useful applications in rheology and many other branches of science and engineering. I see the beauty of closure in this association with recognizing, highlighting and formulating the essentials, as I want to elaborate in this article. I try to offer some colorful tesserae which, hopefully, the reader can use to compose an appealing mosaic of the role of closure in the process of understanding.

II. THE BEGINNING: DIFFERENTIAL CONSTITUTIVE EQUATIONS

The origin of rheology as a scientific discipline lies in the 1920s when Eugene C. Bingham coined the term *rheology* (1920) and the *Society of Rheology* was founded (1929). Closure, in a wide sense, has been a central topic of rheology ever since the derivation of the convected Maxwell model from molecular considerations by Green and Tobolsky (1946) and the famous formulation of differential rheological equations of state by Oldroyd (1950). Differential constitutive equations for the stress tensor have a long and successful history in rheology [see, for example, Bird, Armstrong and Hassager (1987)]. Such constitutive equations successfully describe a variety of nonlinear viscoelastic phenomena in a simple setting, and hence they contribute significantly to our understanding in rheology.

The flow behavior of Newtonian fluids can be described in terms of the five hydrodynamic field of mass density, velocity (three components), and temperature (instead of the velocity, one can use the momentum density and, instead of the temperature, one can use the internal energy or entropy density). This is a natural, universal setting suggested by conservation laws. What is the minimum setting for an autonomous description of more complex fluids? For rheologists, it seems natural to employ the stress tensor as an important further variable, and the search for differential constitutive equations expresses the belief that, with the stress tensor alone, one can obtain a closed description of complex fluids. An additional *tensor as a structural variable* provides a classical setting for the autonomous description of complex fluids in rheology.

While we rheologists grew up with differential rheological equations of state, the possibility of formulating realistic equations of this type is not *a priori* obvious. The primary source of stresses are forces acting over distances, and the stress tensor can be expressed as the average of a tensor product of relative position and force vectors [Irving and Kirkwood (1950)]. A differential equation of state implies the possibility of finding a closed description for such an average. Describing complex fluids with just an additional tensor always implies a closure assumption for an average of some tensor product of two vectors. This becomes more obvious when one tries to derive differential equations of state from kinetic theory [Bird, Curtiss, Armstrong and Hassager (1987)] as, for example, in the classical work by Peterlin (1961, 1966) on nonlinear springs. Kinetic theory also explains why it may be more natural and convenient to work with a conformation tensor, such as the second moment of

a dumbbell vector, rather than with the stress tensor directly. Of course, the stress tensor must then be expressed in terms of the conformation tensor [Dressler et al. (1999)].

In a wider sense, any choice of an autonomous level of description admitting a closed description requires some form of closure assumption. For example, when generalizing from dumbbell models of polymer solutions to bead-spring-chain models one looks for closure in a whole array of conformation tensors, where Gaussian approximations are particularly popular and successful. Models with two coupled tensor variables have also been motivated by abstract orientation and elongation tensors [Wilchinsky et al. (2001)] or by the successful fitting of rheological data [Edwards et al. (1996)]. It is natural to include the heat flux in the same way as the momentum flux into the list of variables. Working with a tensor and a vector is hence another natural scenario [Müller (1967); Beris and Edwards (1994); Jou et al. (1996); Jou et al. (1998); Jou and Casas-Vázquez (2001); Lebon et al. (2008)] which is useful not only for complex fluids undergoing non-isothermal flow but also to formulate relativistic hydrodynamics [Öttinger (1998*b,c*)]. The entire framework of *extended irreversible thermodynamics* has been built on the idea to employ the momentum and heat fluxes as additional structural variables [Jou et al. (1996); Jou et al. (1998); Jou and Casas-Vázquez (2001); Lebon et al. (2008)]. The level of a tensor and a scalar has been analyzed in its general form in Öttinger (2002) because it has found a number of modern applications, for example, in the Doi-Ohta model of emulsions and blends [Doi and Ohta (1991); Wagner et al. (1999)], where the scalar describes the amount of interface per unit volume and the tensor variable separately accounts for the orientation of the interface, or in the pompon model for melts of branched polymers [McLeish and Larson (1998); Öttinger (2001)], where the scalar represents the stretch of a tube confining the molecular backbone and the tensor is used to characterize the tube orientation, or in transient network models of polymer melts, where the scalar describes the number density of network segments and the tensor characterizes the segment deformation. An even simpler example is provided by inhomogeneous dilute polymer solutions [Öttinger (1992); Beris and Mavrantzas (1994)], where the scalar describes the polymer concentration and the tensor represents the polymer stretch and orientation.

In all the above-mentioned theories with a tensor variable, underlying closure assumptions must exist, at least, if one models nonlinear effects. The success of differential equations of state suggests not to consider closure as a necessary evil but as an important step toward grasping the qualitative essence of rheological phenomena. If one thinks about the Doi-Ohta

or pompon models one appreciates the understanding of the rheological behavior of complex systems based on the evolution of structural variables, and one does not at all worry about closure approximations. As a matter of fact, closure creates comprehension.

III. THERMODYNAMIC STRUCTURE

To understand the essence of rheological and other nonequilibrium properties, one should formulate equations on as coarse as possible levels of description. Passing to a coarser level of description should not be regarded as a formal mathematical approximation but rather as an insightful physical identification of the relevant variables, that is, as an intellectual achievement. We are then faced with the following question: *What are the fundamental physical principles that should be respected in formulating an evolution equation on any autonomous level of description?* This is, of course, the realm of nonequilibrium thermodynamics. In the ideal case, the fundamental thermodynamic structure enforces not only physically admissible but also mathematically well-behaved equations for which the existence and uniqueness of solutions can be demonstrated. The thermodynamic structure should also be preserved in numerical integration schemes.

After respecting all conservation laws, the most prominent thermodynamic principle is certainly the second law excluding the possibility of a negative entropy production rate. Also the clear separation of reversible and irreversible contributions to evolution equations is of fundamental importance. The reversible contribution should possess a rich structure reflecting the idea of “mechanistic control,” and it should not touch the entropy. The reversible contribution is generally assumed to be of the Hamiltonian form and hence requires an underlying geometric structure (given in terms of a Poisson bracket or Poisson operator). The remaining irreversible contribution is driven by the nonequilibrium entropy by means of a dissipative bracket. In the GENERIC (“general equation for the nonequilibrium reversible-irreversible coupling”) framework of nonequilibrium thermodynamics [Grmela and Öttinger (1997); Öttinger and Grmela (1997); Öttinger (2005)], these ideas are condensed into the evolution equation

$$\frac{dx}{dt} = L \cdot \frac{\delta E}{\delta x} + M \cdot \frac{\delta S}{\delta x}, \quad (1)$$

where x represents the set of independent variables required for a complete description of a given nonequilibrium system, E and S are the total energy and entropy expressed in terms

of the system variables x , and L and M are certain linear operators, or matrices, which can also depend on x . Equation (1) is supplemented by the complementary degeneracy requirements

$$L \cdot \frac{\delta S}{\delta x} = 0, \quad (2)$$

and

$$M \cdot \frac{\delta E}{\delta x} = 0. \quad (3)$$

The requirement that the entropy gradient $\delta S/\delta x$ is in the null-space of L in Eq. (2) expresses the reversible nature of the L -contribution to the dynamics: the functional form of the entropy is such that it cannot be affected by the operator generating the reversible dynamics. The requirement that the energy gradient $\delta E/\delta x$ is in the null-space of M in Eq. (3) expresses the conservation of the total energy in a closed system by the M -contribution to the dynamics. The two contributions to the time-evolution of x generated by the energy E and the entropy S in Eq. (1) are called the reversible and irreversible contributions, respectively.

Further general properties of the matrices L and M are discussed most conveniently in terms of the Poisson and dissipative brackets

$$\{A, B\} = \frac{\delta A}{\delta x} \cdot L \cdot \frac{\delta B}{\delta x}, \quad (4)$$

$$[A, B] = \frac{\delta A}{\delta x} \cdot M \cdot \frac{\delta B}{\delta x}, \quad (5)$$

where A, B are sufficiently regular real-valued functions on the space of independent variables. In terms of these brackets, Eq. (1) and the chain rule lead to the following time-evolution equation of an arbitrary function A in terms of the two separate generators E and S ,

$$\frac{dA}{dt} = \{A, E\} + [A, S]. \quad (6)$$

The further conditions for L can now be stated as the antisymmetry property

$$\{A, B\} = -\{B, A\}, \quad (7)$$

and the Jacobi identity

$$\{A, \{B, C\}\} + \{B, \{C, A\}\} + \{C, \{A, B\}\} = 0, \quad (8)$$

whereas the product or Leibniz rule for Poisson brackets,

$$\{AB, C\} = A\{B, C\} + B\{A, C\}, \quad (9)$$

follows immediately from the definition in Eq. (4). In these equations, C is another arbitrary sufficiently regular real-valued function on the state space. These properties are well-known from the Poisson brackets of classical mechanics, and they capture the essence of reversible dynamics. The Jacobi identity (8), which is a highly restrictive condition for formulating proper reversible dynamics, expresses the invariance of Poisson brackets in the course of time (*time-structure invariance*).

Further properties of M can be formulated in terms of the symmetry condition

$$[A, B] = [B, A], \quad (10)$$

and the non-negativeness condition

$$[A, A] \geq 0. \quad (11)$$

This non-negativeness condition, together with the degeneracy requirement (2), guarantees that the entropy is a nondecreasing function of time,

$$\frac{dS}{dt} = \frac{\delta S}{\delta x} \cdot M \cdot \frac{\delta S}{\delta x} = [S, S] \geq 0. \quad (12)$$

The properties (10) and (11) imply the symmetry and the positive-semidefiniteness of M [for a more sophisticated discussion of the *Onsager-Casimir symmetry* properties of M , see Sections 3.2.1 and 7.2.4 of Öttinger (2005)]. From a physical point of view, M may be regarded as a friction matrix.

The thermodynamic structure summarized here can also be regarded as a *geometric structure*. In the mathematical literature, this geometric structure is sometimes referred to as *metriplectic* [Morrison (1986)]. In particular, Poisson operators are intimately related to (duals of) Lie algebras [see, for example, Appendix B of Öttinger (2005) or Marsden and Ratiu (1999)]. For example, convection effects are related to the Lie group of space transformations and its representations; as a result, we obtain convected rather than partial time derivatives, as required by the famous principle of *material objectivity* or *frame indifference* [Bird, Armstrong and Hassager (1987); Lodge (1974)].

IV. DOI AND BINGHAM CLOSURES

We now have the thermodynamic tools to address the topic of closure thoroughly. One of the most famous closures in rheology is the quadratic *ansatz*

$$-\dot{\gamma} : \langle \mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u} \rangle = -\dot{\gamma} : \langle \mathbf{u}\mathbf{u} \rangle \langle \mathbf{u}\mathbf{u} \rangle \quad (13)$$

introduced by Doi in the theory of liquid crystal polymers [Doi (1981)]. The Hess-Doi theory of liquid crystal polymers [Hess (1976), Doi (1981)] is based on a configurational distribution function $f(\mathbf{u})$ for an ensemble of rigid rods, where \mathbf{u} is the orientation vector of a rod. The averages in Eq. (13) are performed with the configurational distribution function $f(\mathbf{u})$. If $\dot{\gamma}$ is the sum of the velocity gradient tensor and its transpose, the left-hand side of Eq. (13) constitutes a convective contribution to the time evolution of the second moment tensor $\langle \mathbf{u}\mathbf{u} \rangle$. As one wishes to obtain a closed evolution equation for $\langle \mathbf{u}\mathbf{u} \rangle$, the fourth moment has to be expressed in terms of second moments, and Eq. (13) offers the simplest possibility. An appealing alternative is to assume

$$\langle \mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u} \rangle = \int \mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u} f_{\langle \mathbf{u}\mathbf{u} \rangle}(\mathbf{u}) d^2u, \quad (14)$$

where $f_{\langle \mathbf{u}\mathbf{u} \rangle}(\mathbf{u})$ is a given class of distribution functions parametrized by the second moments [Chaubal and Leal (1998); Feng et al. (1998)]. The most popular choice is the exponential of a quadratic form of \mathbf{u} , the mathematical-statistical properties of which have been studied by C. Bingham (1974) (who should not be confused with the pioneering rheologist Eugene C. Bingham).

The idea of introducing *parametric distributions* to obtain closure is widely used in nonequilibrium statistical thermodynamics. Generalized canonical distribution functions parametrized by Lagrange multipliers are obtained by maximizing the entropy under constraints [Ilg et al. (2002); Ilg et al. (2003)]. For example, the Bingham distribution arises by maximizing the entropy for a fixed second-moment tensor [Ilg et al. (2003)]. The derivative of the entropy with respect to the second-moment tensor is then given by $k_B \mathbf{\Lambda}$, where $\mathbf{\Lambda}$ is the Lagrange multiplier associated with $\langle \mathbf{u}\mathbf{u} \rangle$ (the Bingham distribution is proportional to $\exp\{-\mathbf{\Lambda} : \mathbf{u}\mathbf{u}\}$). Efficient integration schemes and accuracy control, with the possibility of changing the level of description upon a loss of accuracy, have been proposed in the manifold of generalized canonical distribution functions [Ilg et al. (2002); Ilg et al. (2003)], which is also known as the quasi-equilibrium manifold. The idea of parametric distributions has been further developed into the powerful tool of the *invariant manifold method* [Gorban and Karlin (1992); Gorban and Karlin (1994); Gorban et al. (2001); Gorban and Karlin (2005)], where geometric ideas and thermodynamic projectors are found to offer a more elegant and general approach to closure problems than explicit parametrizations, and an iterative Newton method conveniently provides successive improvements of

the equations for the moments. However, the invariant manifold method cannot produce any dissipation; in particular, it cannot produce irreversible equations from reversible ones. To allow for this possibility, the method has been enhanced by *Ehrenfest coarse graining* [Gorban et al. (2001); Gorban and Karlin (2005)].

The closure approximations (13) and (14), among many others, have been studied intensely in the literature on the rod model of liquid crystal polymers [Hinch and Leal (1976); Doi (1981); Doi and Edwards (1986); Advani and Tucker III (1990); Larson (1990); Larson and Öttinger (1991); Bhave et al. (1993); Chaubal et al. (1995); Chaubal and Leal (1998); Feng et al. (1998); Ilg et al. (1999); Edwards (2002); Forest and Wang (2003); Kröger et al. (2008)]. Some of these closures are extremely successful in particular flow situations but fail terribly in others. For example, in simple shear flow, Doi’s quadratic closure (13), when applied to the fourth moments occurring both in the reversible and in the irreversible terms, exhibits only time-independent stable solutions [Bhave et al. (1993); Chaubal et al. (1995)] and thus misses the well-known periodic solutions known as “tumbling” (preferred axis of alignment rotates in the plane of shear) and “wagging” (preferred axis oscillates back and forth in the plane of shear), whereas the Bingham closure admits such time-dependent stable solutions. Can one identify the ultimate winners and losers by such observations so easily?

At this point, we should remember our goals and ambitions. We are not really interested in the Olympic Games of mathematical closure approximations, in which gold, silver, and bronze medals are given away in a myriad of specialized flow disciplines. We rather strive after fundamental understanding by identifying and verifying autonomous levels of description bringing out the essence of a problem, without necessarily reproducing all the details. In the present case, the autonomous level of description for liquid crystal polymers is proposed to be given by the structural variable $\langle \mathbf{u}\mathbf{u} \rangle$, and we must respect the structure of thermodynamically admissible equations on this level. Moreover, judging the success of closure approximations by a comparison with the exact results for all kinds of flow situations is not particularly useful; we should clearly prefer to find *a priori* criteria for overall success that do not require any knowledge of exact solutions.

As the fourth moment in Eq. (13) is associated with convection, we deal with a reversible term generated by the energy gradient with the help of a Poisson operator. As the kinetic energy, which generates convection, is unaffected by the structural variable, we need to

focus on the Poisson operator and its properties as the hallmarks of reversible motion under mechanistic control. The most restrictive criterion is the Jacobi identity (8) expressing the time-structure invariance of reversible dynamics. This criterion has been analyzed in great detail in a similar context by Edwards and Öttinger (1997), and we here merely summarize and discuss the most important results.

According to Edwards and Öttinger (1997), reversible dynamics obtained under the Doi closure (13) can be generated by a valid Poisson operator, whereas this is impossible for the Bingham closure (14) and many other common closures. The analysis of Edwards and Öttinger (1997) proceeds according to symmetry. Note that the fourth moment is symmetric in all four tensor indices. This full symmetry, which is respected by the Bingham closure, is incompatible with time-structure invariance. The Doi closure possesses symmetry in pairs of indices, and under exchanging the pairs. For this lowered level of symmetry, the Doi closure (13) is the only possible closure compatible with time-structure invariance. For even lower levels of symmetry, further admissible closures can be constructed [Edwards and Öttinger (1997)].

Of course, you could say “Why should I, as a rheologist, make my life more complicated by worrying about some mysterious Jacobi identity?” Because Poisson structures are at the heart of reversible dynamics, and because violating laws out of ignorance does not protect you from punishment! Of course, one could still try to argue why a law is not applicable in a particular situation, but the only reason for losing mechanistic control in reversible dynamics that I am currently aware of is the presence of nonholonomic constraints.

If one has to *choose or compromise between symmetry and time-structure invariance*, why should symmetry be less important? The answer should be clear by now: Because our goal is to establish a healthy autonomous level of description based on second moments, consistent with all the laws of nonequilibrium thermodynamics, and not necessarily to achieve a faithful mathematical approximation of a fourth moment in terms of second moments.

If only the quadratic closure (13) is thermodynamically admissible, does thermodynamics thus force us into an inferior closure that cannot even predict “tumbling” and “wagging” in shear flow? A much more balanced view was offered by Bhave et al. (1993), Chaubal et al. (1995), Chaubal and Leal (1998), and Feng et al. (1998), based on a “solution map” or “bifurcation set” in the parameter space of two-dimensional flows and nematic strength. *Shear flow appears as a singular special case*, and “tumbling” and “wagging” do actually

occur within the quadratic closure for flows that are only very slightly more rotational than simple shear flow. The overall solution map is deformed only slightly for the quadratic closure, but with rather serious consequences for the singular special case of shear flow. Moreover, none of the known closures exhibiting “tumbling” and “wagging” can predict the proper transition from “wagging” to flow aligned steady solutions at high shear rates [Feng et al. (1998)].

A more rotational behavior with “tumbling” and “wagging” can also be achieved by going from the upper convected codeformational derivatives appearing naturally in the second moment equations to mixed or Schowalter derivatives [see pp. 556 and 568 of Beris and Edwards (1994)]. It has been elaborated in Section 4.2.3 of Öttinger (2005) that, within the GENERIC framework, such a modification can be implemented through an additional irreversible contribution, as suggested by the occurrence of a slip coefficient. Schowalter derivatives are represented by an antisymmetric contribution to the friction matrix so that, according to Eq. (12), they do not lead to entropy production.

We have focused entirely on the fourth moment (13) that appears as a convective contribution to the time evolution of the second moment tensor $\langle \mathbf{u}\mathbf{u} \rangle$. We have not paid any attention to the fact that, for the Maier-Saupe mean-field nematic potential, there occurs another fourth moment in the irreversible contribution to that evolution equation so that a further term requires closure. As a matter of fact, a different closure could be used there because irreversible contributions are much less restricted than reversible ones. For example, one could use the Doi closure in the reversible contribution to fulfill time-structure invariance, and the more symmetric Bingham closure in the irreversible contribution in order to combine the advantages of both closures [Sgalari et al. (2002)], where the less restricted closure in the irreversible term seems to be the bigger source of problems. Actually, the fact that the GENERIC framework of thermodynamics expresses time evolution in terms of the generators E , S and the matrices L , M strongly suggests to consider each of these building blocks separately, that is, with the natural possibility of *separate closures in the reversible and irreversible terms*. In the subsequent section, we look at the implications of thermodynamics for closure in the irreversible contribution to the time evolution of moments. We do this in the context of the Gaussian approximation, which has found many successful applications in polymer kinetic theory. The rod model of liquid crystal polymers could be investigated in a similar way, but the handling of Gaussian distributions is more familiar.

V. GAUSSIAN CLOSURE

In the Gaussian closure procedure, or Gaussian approximation, the Jacobi identity is not an issue. Because there are no constraints and Gaussian objects are deformable, one can realize codeformational behavior in the form of upper convected derivatives, which are known to be consistent with a Poisson bracket [Öttinger (2005)]. Nevertheless, something remains to be checked for the irreversible term. As Gaussian approximations are usually implemented on the level of time-evolution equations, one needs to check whether they are consistent with a Gaussian entropy generating irreversible dynamics via the friction matrix obtained for Gaussian distributions according to Eq. (1).

To discuss the proper formulation of the irreversible term in the Gaussian approximation, we start from a Fokker-Planck equation of the general form

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial x_j} \left(A_j - \frac{1}{2} D_{jk} F_k \right) f + \frac{1}{2} \frac{\partial}{\partial x_j} D_{jk} \frac{\partial}{\partial x_k} f \quad (15)$$

where $f = f(x)$ is a probability density in some K -dimensional space with coordinates x_j , A_j is a reversible drift vector, the positive-semidefinite symmetric diffusion matrix D_{jk} describes the irreversible effects,

$$F_j = -\frac{\partial \ln f^{\text{eq}}}{\partial x_j} \quad (16)$$

is the effective force implied by the equilibrium probability density f^{eq} , and Einstein's summation convention is assumed (one needs to sum from 1 to K over all indices occurring twice). We look for (because we believe in the adequacy of) a description on the level of a matrix c of second moments with entries,

$$c_{ij} = \langle x_i x_j \rangle = \int x_i x_j f d^K x, \quad (17)$$

where the coordinates x_j are assumed to be introduced such that $c_{ij}^{\text{eq}} = \delta_{ij}$. We further assume that the first moments vanish for symmetry reasons. In the Gaussian approximation, these assumptions imply $F_j = x_j$.

The entropy on the level of second moments can be obtained by evaluating the Boltzmann-type conformational entropy $-k_B \int f \ln(f/f^{\text{eq}}) d^K x$, where k_B is Boltzmann's constant, for Gaussian distributions. The result is [see, for example, Exercise 66 of Öttinger (2005)]:

$$S = \frac{1}{2} k_B (K - c_{jj} + \ln \det c), \quad (18)$$

with the derivative

$$\frac{\partial S}{\partial c_{ij}} = \frac{1}{2} k_B (c_{ij}^{-1} - \delta_{ij}). \quad (19)$$

Equation (18) for the entropy is an essential feature of any Gaussian approximation.

For the explicit transformation rule (17) from probability densities f to second moments $\langle x_i x_j \rangle$, one can transform the friction matrix M occurring in the irreversible contribution to the Fokker-Planck equation (15) according to Eq. (6.180) of Öttinger (2005). The result is:

$$2k_B M_{ij,kl} = \langle x_i x_k D_{jl} \rangle + \langle x_i x_l D_{jk} \rangle + \langle x_j x_k D_{il} \rangle + \langle x_j x_l D_{ik} \rangle. \quad (20)$$

All four contributions on the right-hand side of this equation are equivalent if $M_{ij,kl}$ is contracted with symmetric tensors; otherwise, the four contributions imply that the contraction should be done with symmetrized tensors only. The Gaussian approximation can now be introduced into Eq. (20) by using Wick's theorem to reduce the order of the moments (see, for example, Eq. (2.61) of Öttinger (1996)). We successively find

$$\langle x_i x_k D_{jl} \rangle = c_{ik} \langle D_{jl} \rangle + c_{mk} \left\langle x_i \frac{\partial D_{jl}}{\partial x_m} \right\rangle, \quad (21)$$

and

$$\langle x_i x_k D_{jl} \rangle = c_{ik} \langle D_{jl} \rangle + c_{mi} c_{nk} \left\langle \frac{\partial^2 D_{jl}}{\partial x_m \partial x_n} \right\rangle. \quad (22)$$

The first term on the right-hand side of each of the Eqs. (21) and (22) represents the effect of a self-consistently averaged diffusion matrix, whereas the second term accounts for fluctuation effects. The description of fluctuation effects by second-order derivatives looks particularly natural. Equation (21) can be rewritten in the alternative form

$$c_{kl}^{-1} \langle x_i x_k D_{jl} \rangle = \langle D_{ij} \rangle + \left\langle x_i \frac{\partial D_{jk}}{\partial x_k} \right\rangle. \quad (23)$$

As we have found the natural entropy and friction matrix for any Gaussian closure, we can now compare to the evolution of the second moments obtained directly from the Fokker-Planck equation (15),

$$\frac{\partial c_{ij}}{\partial t} = \langle A_i x_j \rangle + \langle x_i A_j \rangle - \frac{1}{2} \langle D_{ik} F_k x_j \rangle - \frac{1}{2} \langle x_i F_k D_{kj} \rangle + \langle D_{ij} \rangle + \frac{1}{2} \left\langle x_i \frac{\partial D_{jk}}{\partial x_k} \right\rangle + \frac{1}{2} \left\langle x_j \frac{\partial D_{ik}}{\partial x_k} \right\rangle. \quad (24)$$

With Wick's theorem in the form of Eq. (23) and the Gaussian property $F_j = x_j$, Eq. (24) can be rewritten as

$$\frac{\partial c_{ij}}{\partial t} = \langle A_i x_j \rangle + \langle x_i A_j \rangle + \frac{1}{2} (\langle x_i x_k D_{jl} \rangle + \langle x_j x_k D_{il} \rangle) (c_{kl}^{-1} - \delta_{kl}). \quad (25)$$

The irreversible contribution to this evolution equation is exactly what one recovers from the irreversible contribution to GENERIC by combining Eqs. (19) and (20). The Gaussian approximation is thus nicely consistent with an irreversible contribution to dynamics generated by the Gaussian entropy on the level of second moments. Contrary to our disappointing experience with the reversible term, parametric density estimation works very nicely for Gaussian approximations to the irreversible term.

In the Gaussian approximation, a configurational distribution function f is assumed to be Gaussian at any time t . This does not necessarily imply a Gaussian stochastic process, for which all joint distributions at different times must also be Gaussian. The construction of a full Gaussian process governed by a linear stochastic differential equation has been described and discussed critically in Section 4.2.4 of Öttinger (1996) and by Hütter et al. (2003). A well-defined and physically consistent stochastic process on the level of second moments can be introduced by adding noise to Eq. (25) according to the fluctuation-dissipation theorem [Hütter et al. (2003)].

Because the Gaussian approximation has been used very successfully in the *kinetic theory of dilute polymer solutions*, where it has been applied to hydrodynamic interactions [Öttinger (1989b); Zylka and Öttinger (1989); Öttinger (1989a); Wedgewood (1989); Prakash and Öttinger (1997)], excluded volume [Prakash and Öttinger (1999); Prabhakar and Prakash (2002); Prakash (2002)], and internal viscosity [Schieber (1993)], we here specialize our general results to the case of bead-spring chains, which has previously been considered by Hütter et al. (2003). If the chains consist of N beads, we have $K = 3(N - 1)$ configurational degrees of freedom and the matrix c is an array of $(N - 1) \times (N - 1)$ tensors \mathbf{c}_{jk} representing the variances and covariances of the $N - 1$ connector vectors, where the normalization condition at equilibrium now reads $\mathbf{c}_{jk}^{\text{eq}} = \delta_{jk}\mathbf{1}$. According to Eq. (18), the conformational entropy per polymer molecule is given by

$$s_{\text{p}} = \frac{1}{2}k_{\text{B}} \left[\sum_{j=1}^{N-1} \text{tr}(\mathbf{1} - \mathbf{c}_{jj}) + \ln \det c \right], \quad (26)$$

where c is the large matrix consisting of $(N - 1) \times (N - 1)$ blocks \mathbf{c}_{jk} , each of which is represented by a 3×3 matrix. As the GENERIC framework involves only derivatives of entropy, we provide the result (19) in the form

$$\frac{\partial s_{\text{p}}}{\partial \mathbf{c}_{jk}} = \frac{1}{2}k_{\text{B}} \left(\mathbf{c}_{jk}^{\text{I}} - \delta_{jk}\mathbf{1} \right), \quad (27)$$

where the tensors \mathbf{c}_{jk}^I are represented by the blocks of the inverse of the large matrix c ,

$$\sum_{l=1}^{N-1} \mathbf{c}_{jl} \cdot \mathbf{c}_{lk}^I = \delta_{jk} \mathbf{1}. \quad (28)$$

The degeneracy condition (2) of nonequilibrium thermodynamics implies that the entropic spring contribution to the pressure tensor is given by

$$\mathbf{\Pi} = n_p T \left\{ s_p \mathbf{1} + \sum_{j,k=1}^{N-1} \left[\mathbf{c}_{jk} \cdot \left(\frac{\partial s_p}{\partial \mathbf{c}_{jk}} \right)^T + (\mathbf{c}_{jk})^T \cdot \frac{\partial s_p}{\partial \mathbf{c}_{jk}} \right] \right\}, \quad (29)$$

where T is the absolute temperature and n_p the number density of polymers. By inserting the derivatives (27) into Eq. (29) and using the symmetry of the large matrix c (which implies $(\mathbf{c}_{jk})^T = \mathbf{c}_{kj}$ and an analogous identity for the inverse), we obtain

$$\mathbf{\Pi} = n_p s_p T \mathbf{1} + n_p k_B T \sum_{j=1}^{N-1} (\mathbf{1} - \mathbf{c}_{jj}). \quad (30)$$

Note that this simple form of the pressure tensor consisting of Hookean spring contributions from each of the connectors is a direct consequence of the functional form of the entropy in Eq. (26).

VI. VARIABLES ARE EVERYTHING

For the development and discussion of the Doi, Bingham, and Gaussian closures in the preceding sections, we looked in great detail at complicated moments and their expression in terms of second moment tensors. Over all these details we should not forget that our sole goal was to establish an autonomous level of description based on second moment tensors. The important questions are: Can this be done? How can this be done? An important outcome of the general analysis of the second-moment level of description is: There is not much choice in the reversible dynamics.

The key problem of nonequilibrium thermodynamics or, if you like, of coarse graining, or of closure, or of understanding, is the choice of good variables for a problem of interest. For this crucial task of choosing variables, thermodynamics leaves you alone with your insight, intuition, imagination, and ingenuity (i⁴). To gain insight, of course, experimental results are of particular importance. Once you have chosen your variables and expressed them in terms of the variables of a more detailed well-established level of description, often

the atomistic level, *statistical thermodynamics provides systematic recipes for calculating the thermodynamic building blocks E , S , L , and M* [Öttinger (1998a); Öttinger (2000); Öttinger (2005); Öttinger (2007); Ilg et al. (2009)]. These building blocks imply the autonomous time evolution (1) and hence all closure properties. The generalized microcanonical, canonical, and mixed ensembles of nonequilibrium statistical mechanics can be considered as natural candidates for parametric density estimation. Any concrete realization of the GENERIC structure provides a solution to the closure problem.

The importance of the choice of variables can be illustrated nicely for the reptation model of melts of entangled linear polymers. One usually does not speak about closure in this context, however, one clearly uses mean-field type and further simplifying assumptions. Starting from the picture of a large number of massively entangled random walk chains, one first assumes that one can look at the motion of a single probe chain constrained by a tube or slip links produced by other chains, or anisotropic friction accounting for the hindrance of sideway motions by other chains. In a second step, the single-chain picture is further reduced to that of a single segment with orientation \mathbf{u} at a position s within the chain, where the label s varies from 0 to 1 in going from one chain end to the other. In order to achieve this further simplification, one needs to make an assumption like “independent alignment of large straight segments” [Doi and Edwards (1978a), Doi and Edwards (1978b), Doi and Edwards (1978c)] or “smooth curvature” [Curtiss and Bird (1981a), Curtiss and Bird (1981b)]. The entanglement length scale is thus introduced as the length of the independently aligned segments or as the persistence length of smoothly curved chains. The truly heroic idea of the reptation model is to postulate that the single-segment configurational distribution function $f(\mathbf{u}, s)$ leads to an autonomous level of description for the complicated system of entangled chains. This postulate implies a natural but highly nontrivial closure.

The formulation of the thermodynamic building blocks, and hence of the evolution equations, is a much simpler step than the choice of variables and can actually be done with very little of i^4 , as has been shown by the author in Section 8.4.6 of Öttinger (2005). Once $f(\mathbf{u}, s)$ has been identified as a good structural variable, there is so much guidance from nonequilibrium thermodynamics that, for example, one is automatically reminded to consider constraint release associated with the reptation of constraining chains and the possibility of anisotropic tube cross sections.

VII. REDUCTION VERSUS COARSE GRAINING

For diffusion equations with Gaussian solutions, which are associated with linear stochastic differential equations, the second-moment equations reproduce all the features of the exact solutions. Closure is usually considered as an approach to achieve approximate solutions to nonlinear problems, with the ambition to be as accurate as possible. This is the idea of a *solution or reduction technique*. In the context of the invariant manifold method, we have already encountered the *hallmark of reduction techniques*: they do not produce any additional dissipation and, in particular, reduction techniques cannot lead from reversible to irreversible equations. Equation (20) for the Gaussian approximation also exhibits the hallmark of reduction: the friction matrix on the level of moments is directly proportional to the diffusion tensor D_{jk} on the level of the configurational distribution function. Also dynamic renormalization, as carried out in the context of hydrodynamic interactions in dilute polymer solutions [Öttinger (2009)], turns out to be a reduction technique.

To illustrate the closure problem in the introduction, we had also mentioned the BBGKY hierarchy and Boltzmann's kinetic equation, where the former is reversible and the latter is irreversible. Boltzmann's derivation of his irreversible kinetic equation for rarefied gases from the reversible equations of classical mechanics is an enormous achievement that has created a lot of controversy and deep insights [Lanford III (1975)]. The derivation of Boltzmann's kinetic equation cannot be achieved by a reduction technique. When new dissipative processes arise in the passage from a more detailed to a less detailed level of description, we speak of a *coarse-graining technique*.

In the case of Boltzmann's kinetic equation, the clear separation of two time scales, namely the duration of collisions and the time between collisions, is at the origin of irreversibility. A detailed analysis of two-particle collisions is required to obtain the Boltzmann equation which itself cannot resolve any processes on the short scale of the duration of a collision. In general, in coarse graining one treats fast processes as fluctuations and fluctuations are associated with dissipation. *Projection operators* provide a powerful tool to separate fast and slow processes, thus providing the statistical mechanics of coarse graining [Zwanzig (1961); Mori (1965a); Mori (1965b); Robertson (1966); Grabert (1982); Öttinger (2005)].

Note that also the diffusion equations for configurational distribution functions used

in polymer kinetic theory themselves are the result of coarse graining. In particular, spring forces between reference points in linear polymer molecules have been discussed by Underhill and Doyle (2004) by means of statistical mechanics in constant extension and constant force ensembles. If, however, one is interested in spring forces between beads, each located at the center of mass of the smaller units coarse grained into the bead, the force laws are different [Laso et al. (1991), Öttinger (2009)].

Both reduction and coarse graining lead to autonomous evolution equations as a result of passing from a more to a less detailed level of description. Both techniques must preserve the GENERIC structure of nonequilibrium thermodynamics, both techniques are associated with closure. Whereas the approximate character of closure may be viewed as a disadvantage in reduction, it is the actual goal of coarse graining: fast processes are eliminated in favor of dissipative processes. This is understanding by focusing on the relevant slow features. One should always try to obtain more transparent equations by coarse graining and only when further coarse graining is impossible, reduction and explicit solution techniques should be used. With the tremendous increase of computer power, there is the temptation of producing numerical solutions without exploiting the full potential of coarse graining. Giving in to this temptation, we miss the opportunity of deeper understanding and, in the long run, our problem-solving skills will deteriorate.

VIII. RHEOLOGY WITHOUT CLOSURE

We have recognized the closure problem, in a wide sense, as the search for autonomous levels of description on which a closed formulation of the evolution of systems is possible. An autonomous system remembers its history, in particular, its flow history, only through the current state of the structural variables of the level of description. There is no explicit memory and the GENERIC evolution equations (1) are pure first-order differential equations.

In rheology, however, also integral rheological constitute equations and memory integral expansions are well-known [Bird, Armstrong and Hassager (1987)]. In view of the enormous possibilities of formulating memory functionals, it is very difficult both to select an appropriate memory functional for a given problem and to formulate the proper thermodynamic principles for memory functionals in general [Coleman and Noll (1963)]. In particular, there is no direct scheme for calculating memory functionals from atomistic models by means of

statistical mechanics. Whereas some established classes of integral models can certainly describe rheological measurements for a variety of systems qualitatively well, and there usually are sufficiently many fitting parameters to get quantitative agreement, there are no systematic ways of translating molecular understanding of a system into successful memory integral models. The identification of key processes and relevant variables, supported by statistical mechanics in evaluating thermodynamic building blocks, is a much more promising pathway to understanding.

Of course, there are connections between differential and integral rheological equations of state or, more generally, between autonomous levels of description and memory functionals. By solving or integrating the evolution equations for the structural variables, in principle, one can determine memory functionals. However, explicit solutions can only be obtained in exceptional (linear) cases. For example, for the reptation model, a deformation measure and a memory function can be identified such that its solution can be written as a simple memory integral; the reptation model of Doi and Edwards has actually been recognized as an integral model of the K-BKZ type [see, for example, Hassager (1981)].

Another famous class of evolution equations with memory are *mode coupling theories*. As the memory effects are included by following well-defined recipes [Götze (1984)], one might like to speak of mode coupling as “quasi-closure.” In particular, mode coupling theory has been found to be useful in the discussion of the glass transition [Götze (1984); Kob and Andersen (1994); Kob and Andersen (1995)]. The glass transition problem is considered to be a very difficult one because the ingenious structural variable for describing it by autonomous evolution equations has not yet been discovered. The potential energy landscape and the inherent structure energy are clearly important concepts [Stillinger and Weber (1982); Angell (1995); Stillinger (1995); La Nave et al. (2003)], and the inherent structure pair correlation function has been proposed as a promising candidate for a coarse grained description of the approach to the glass transition [Öttinger (2006)]. This idea has actually revealed a static signature of the onset of the glass transition [Del Gado et al. (2008)]. Structural variables associated with “shear transformation zones” may be an interesting alternative [Falk and Langer (1998)].

IX. CLOSURE

We have offered some reflections on the topic of closure which strongly suggest that closure should not be considered as a helpful mathematical approximation but as the cornerstone of establishing autonomous levels of description. Choosing good structural variables is the physical prerequisite to achieve closure and to perform successful coarse graining, that is, to elaborate the essential features of problems. Closed simplified descriptions lead to understanding. We have illustrated this situation in the context of the highly restricted fourth-moment closure in the convection term of the rod model of liquid crystal polymers, of the admissibility of Gaussian closures in the irreversible term for bead-spring models of dilute polymer solutions, and of the far-reaching ingenuity of the variables in the reptation model of melts of entangled linear polymers. Liquid crystals and Gaussian closures provide examples of reduction, that is, approximate solution procedures. Even more revealing is closure obtained from a coarse graining procedure, which replaces fast processes by dissipative ones, such as the reptation process.

With mild exaggeration (rooted in enthusiasm rather than one-sidedness), our reflections on closure can be expanded into a full world-map of rheology. The milestones of theoretical rheology are ground-breaking new models, and these come with and actually *via* the insightful and revealing discovery of good variables. Then, closed equations can be formulated on the corresponding autonomous level of description. Nonequilibrium thermodynamics provides the structure of admissible evolution equations, nonequilibrium statistical mechanics offers the recipes for finding concrete realizations of the thermodynamic structure for given variables. We thus obtain all rheological information for the system defined through the ingeniously chosen variables.

Internal energy and entropy are key concepts in nonequilibrium thermodynamics. This clearly indicates the way to go for rheology. Focusing on the momentum balance and momentum flux has been a good starting point, but a detailed investigation of the associated entropy flux must be the next step. This also requires consideration of compressibility effects. How do we need to generalize the concepts of thermal conductivity and heat capacity in complex fluids undergoing flow? Pioneering experiments on anisotropic heat flow have been performed by Venerus, Schieber and coworkers [Venerus et al. (1999); Broerman et al. (1999); Iddir et al. (2000); Venerus et al. (2004); Schieber et al. (2004);

Balasubramanian et al. (2005)], and some issues associated with generalizing the concept of heat capacity have been discussed by Hütter et al. (2009).

Nonequilibrium thermodynamics guides the formulation of autonomous evolution equations and offers the recipes for finding the thermodynamic building blocks on a less detailed level of description from a more detailed level of description. The thermodynamic structure is a geometric one and the passage between different levels of description hence is a mathematical topic of structure preserving transformations [Öttinger and Struchtrup (2007)]. Ideally, the relationship between thermodynamics and mathematics should be even more intimate. For example, general mathematical results concerning asymptotic stability have already been obtained for metriplectic, or GENERIC, structures by Birtea et al. (2007). The criteria for thermodynamic admissibility, in particular, the existence of a nondecreasing entropy and a positive semidefinite friction matrix, should coincide with the criteria for mathematically proving the existence and uniqueness of solutions to the evolution equations. The existence of unique solutions is what we expect from meaningful equations. Thermodynamics shall be designed to guarantee that.

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